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PRODUCTS HAVING MULTIPLE-SUBSTITUTED  
POLYSILOXANE MONOLAYER

The present invention relates to providing

5 specialized polysiloxane coatings to articles. The coatings provide protective attributes to the substrates bearing the coatings, without loss of and in some cases with enhancement of the desirable properties of the substrates.

- 10 The present invention relates in particular to the formation of specialized siloxane monolayers on substrates which are susceptible to damage upon exposure to acidic environments or basic environments, or which are vulnerable to physical degradation such as cracking.
- 15 The invention relates in particular to the provision of such monolayers on silica-based chromatographic supports, in order to protect such supports from damage due to the ambient chemical environment while retaining the desirable chromatographic properties of the support.
- 20 The invention also relates to providing such monolayers to glassware and glass surfaces, to provide desired protection as described hereinbelow.

- While it has generally been known to apply "silicone" coatings to articles to impart various
- 25 protective properties, such as waterproofing, it is believed herein to be novel to adjust the substituents on the silicon atoms making up such coatings in order to favorably affect the properties of the coating and of the articles bearing the coating. In addition,
- 30 providing such adjustment on "coatings" which are in reality monolayers of siloxanyl (that is, -Si-O-) based monolayers is believed to be all the more novel.

1           Chromatographic packings can comprise silica  
gel to which organic substituents, such as alkyl chains,  
have been attached. It has heretofore been accepted  
that the susceptibility of such materials to attack by  
5 acids or bases has been an unavoidable concomitant of  
the packing's ability to perform properly in  
chromatographic applications. Thus, modification such  
as that which is the subject of the present invention  
has not been considered.

10           Indeed, formation of a siloxanyl monolayer  
might be expected to interfere with properties such as  
chromatographic capabilities because it would alter the  
shape and size of pores and would affect other surface  
characteristics.

15           For instance, a published abstract with  
respect to Japanese Patent Application No. 61287444  
describes porous silica particles characterized in that  
the inner surfaces of the pores carry a hydrophobic  
layer formed by a reaction of the silica in the pore  
20 with an alkyl or aryl halosilane, among which are listed  
octadecyltri-chlorosilane and propyltrichlorosilane,  
among others, wherein the remaining exposed surface of  
the silica particle is bonded to hydrophilic groups such  
as ethylene glycol, glycerol, sorbitol, polyethylene  
25 oxide, glycidoxypropyltrimethoxy-silane,  
ethyleneglycolmono-ethylether, or diethyleneglycol. The  
abstract does not disclose the formation of a siloxanyl  
monolayer, nor is there disclosed any intimate  
intermingling of different substituents on adjacent  
30 silicon atoms; indeed, such a product would be directly  
contrary to the teachings of this abstract which

1 requires substituents of various types at quite distinct  
locations on the silica particle.

A number of other sources disclose bonding  
various substituents to an oxide surface, particularly a  
5 silica surface, but none discloses or suggests providing  
multiple distinct substituents at adjacent or nearly  
adjacent sites on a siloxanyl monolayer. Examples  
wherein the substrate is glass or a chromatographic  
surface include U.S. Defensive Publication T958,010,  
10 U.S. Patent No. 4,755,294, U.S. Patent No. 4,604,207,  
and U.S. Patent No. 4,512,898. Other publications  
examining the formation of alkyl-substituted siloxanyl  
monolayers on silica gel are typified by P. Silberzan,  
et al., in Langmuir, Vol. 7, No. 8, pp. 1647-1651 (1991)  
15 and S. Wasserman, et al., in J. Am. Chem. Soc., Vol.  
111, No. 15, pp. 5852-5861 (1989).

Briefly stated, one aspect of the present  
invention is a product to which is chemically bonded a  
monolayer of silicon atoms which are connected to other  
20 silicon atoms in said monolayer through oxygen atoms in  
said monolayer, wherein the monolayer is substituted  
with a first hydrocarbyl substituent and a second  
hydrocarbyl substituent and each of the silicon atoms in  
said monolayer is substituted with said first  
25 hydrocarbyl substituent or said second hydrocarbyl  
substituent, wherein said first hydrocarbyl substituent  
is longer than said second hydrocarbyl substituent.

In another aspect of the present invention,  
the product is silica gel or another inorganic oxide, or  
30 a substrate whose surface is silica gel or such other  
inorganic oxide, and the first and second hydrocarbyl  
substituents are selected such that the substrate

1 bearing the substituted monolayer is useful as, for  
instance, a chromatography column, and exhibits a high  
degree of resistance to acidic and basic attack. Yet  
another aspect of the present invention is the use of  
5 such a product in chromatography.

Yet another aspect of the present invention is  
glass, such as glass articles, glassware, glass optical  
fibers, glass capillaries, and the like, bearing the  
monolayer described herein, wherein the monolayer  
10 protects the surface of the glass from acidic and basic  
environments and from physical degradation such as  
cracking.

While the present invention is particularly  
useful in the preparation of products comprising silica  
15 which bears the monolayer described herein, the present  
invention is believed to be useful in providing the  
indicated protection against chemical degradation to a  
large variety of materials. Stated generally, any  
product having a surface which reacts with alkyl  
20 trichlorosilane to bond to the silane, can be provided  
with a monolayer in accordance with the present  
invention. Preferred materials are characterized in  
that they comprise surface oxygen. By "surface oxygen"  
is meant that the material contains, at its surface,  
25 oxygen which is covalently (or, in certain embodiments,  
ionically) bound in the material, which oxygen is  
capable of being covalently bonded to silanes. More  
specifically, the surface oxygen is considered within  
the scope of this aspect of the invention if the oxygen  
30 reacts with any alkyl trichloro-silane to form O-Si  
bonds.

1 Preferred materials to which the monolayer is  
applied include silica gel, silica-based glass and  
glassware, and optical "fiber optic" cable, as well as  
materials comprising oxides or mixed oxides of any  
5 inorganic material whose oxide is solid at standard  
temperature and pressure. Also included are carbonates,  
aluminosilicates, silicates and phosphates, of any  
inorganic cation. Also included are materials in which  
two or more of these are chemically combined or  
10 physically blended. Examples of the foregoing include  
inorganic pigments, limestone and clays (which typically  
comprise aluminosilicates). Additional examples include  
any inorganic element and oxides thereof so long as the  
surface thereof is capable of forming bonds to silicon  
15 atoms in the monolayer. Examples include but are not  
limited to alumina, zirconia, beryllia, titanium  
dioxide, magnesium oxide, and oxides of vanadium,  
chromium, manganese, iron, cobalt, nickel, copper, zinc,  
gadolinium, germanium, arsenic, rubidium, strontium,  
20 yttrium, niobium, molybdenum, ruthenium, rhodium,  
platinum, gold, silver, thallium, lead and bismuth.

One preferred embodiment of the present  
invention is silica gel or a substrate of a different  
material having a silica gel surface. The monolayer  
25 provides a protective layer to the silica gel.

The invention finds particular usefulness in  
chromatographic applications, including not only silica-  
based chromatographic supports but also metal-oxide  
chromatographic substrates.

30 Another preferred embodiment of the present  
invention is glass articles, such as glassware,  
capillary tubes, optical fibers, windows and windshields

- 1 (whether for conventional construction and vehicular applications or more specialized uses in reactors and spacecraft), and any other article having a glass outer and/or inner surface. Providing the monolayer to
- 5 glassware will help protect against acidic and basic environments, and will help resist the microscopic chemical and mechanical processes at the glass surface that help initiate and propagate cracking and related degradation. Providing the monolayer to optical fibers
- 10 and inner spaces such as capillaries will likewise protect the inertness of the glass surface to acidic and basic attack and to mechanical degradation. Capillary tubes thus treated are useful in capillary chromatography and capillary electrophoresis.
- 15 Of particular interest is the embodiment wherein a surface comprising zirconium oxide (per se or alloyed) is treated in accordance with the present invention to provide protection from the aggressive environment to which the zirconium-based materials are
- 20 exposed when they are used as moderators in pressured-water nuclear power reactors. Preferred groups to provide on such an oxidic surface are lower alkyl, such as methyl, and di-hydroxy lower alkyl, such as  $\text{HOCH}_2\text{-CH(OH)-CH}_2\text{-}$ .
- 25 As indicated, the monolayer is formed of silicon atoms bound to the substrate surface and connected to each other through single oxygen atoms. In addition, the monolayer is characterized in that it is substituted with the first and second hydrocarbyl
- 30 substituents described herein. Each of the silicon atoms forming the monolayer is substituted with either a first hydrocarbyl substituent or a second hydrocarbyl

1 substituent. In the broadest aspect of the present  
invention, there may be regions of the monolayer in  
which the first hydrocarbyl substituent predominates,  
even to the exclusion of the second hydrocarbyl  
5 substituent, and vice versa. However, in the preferred  
embodiment the first and second hydrocarbyl substituents  
are both distributed essentially uniformly across the  
surface of the monolayer. While it will be recognized  
that totally unvarying distribution of the first and  
10 second substituents on the monolayer may not be  
achieved, the product will generally preferably be  
characterized in that each of the first and second  
substituents are distributed essentially uniformly, or  
as nearly uniformly as possible, on the surface of the  
15 monolayer. In that way, the relative proportions of the  
first and second substituents will be essentially  
constant at any region on the monolayer.

The first and second hydrocarbyl substituents  
are preferably selected to optimize the property or  
20 properties desired of the product which will bear the  
monolayer, and to ensure the provision of a protective  
coating to the surface of the article. In the aspect of  
the present invention in which the desired property is  
the ability to carry out effective chromatographic  
25 separation when the article is used as a packing  
material for, e.g., HPLC or other gas-phase  
chromatography, the first hydrocarbyl substituent should  
be one which assists in providing chromatographic  
separation when bound to a chromatographic support.  
30 Examples of such substituents will be familiar to those  
conversant with the field of chromatography, and are  
indeed quite numerous. Examples include phenyl;

- 1 epoxide; alkyl, containing from 1 to 60 carbon atoms in the longest chain, preferably 1 to 30 and more preferably 3 to 18 atoms in the longest chain; monounsaturated alkylene containing 2 to 60 carbon atoms
- 5 in the longest chain; or derivatives in which alkyl or monounsaturated alkylene containing up to 60 carbon atoms contains one or more (preferably up to 12) hetero linkages such as -O-, -N(R)-, -S-, -C(O)-, -SO<sub>2</sub>-, -C(O)O-, -OC(O)-, -C(O)N(R)-, or -N(R)C(O)-. The
- 10 phenyl, alkyl and alkylene may optionally be substituted with one or more of hydroxyl, halogen (particularly fluorine, chlorine or bromine, especially fluorocarbons), cyano, nitro, -COOH, -SO<sub>3</sub>H, -N(R)(R), -R<sup>1</sup>Si(R<sup>2</sup>)<sub>3-n</sub>(OH)<sub>n</sub> wherein n is 1, 2 or 3, wherein R<sup>1</sup> and
- 15 R<sup>2</sup> are each alkyl, alkoxy or alkylene containing up to 6 carbon atoms, and preferably methyl, ethyl, methoxy or ethoxy; or straight or branched lower alkyl containing up to 6 carbon atoms (which lower alkyl may be substituted with any of the foregoing substituents),
- 20 wherein R at each occurrence is hydrogen or alkyl containing 1 to 6 carbon atoms. Thus, -N(R)(R) can be amino, monoalkylamino, or dialkylamino. Thus, exemplary functional groups include diol (such as HOCH<sub>2</sub>-CH(OH)CH<sub>2</sub>-), polyamine, carboxylic acid, sulfonic
- 25 acid, and (N-trimethoxysilylpropyl) polyethyleneimine.

A preferred first substituent is alkyl containing 2 to 24 carbon atoms, and more preferably octadecyl. Preferred embodiments in which the alkyl chain has a substituent are those in which the

30 substituent is in the omega-position. Another preferred first hydrocarbyl substituent has terminal ethylenic unsaturation. Examples include CH<sub>2</sub>=CHCH<sub>2</sub>-, and more



1 generally  $\text{CH}_2=\text{CH}-(\text{CH}_2)_{1-24}$ -. The unsaturated group is  
useful in that other molecules that react with  $-\text{CH}=\text{CH}_2$   
groups can be attached to the hydrocarbyl substituent at  
that site. Epoxide groups and hydride groups, when  
5 present attached to the hydrocarbyl substituents, can  
also serve as sites to which other molecules and  
functional groups can be attached. Examples of such  
molecules include ones that impart hydro-phobicity or  
color, or which serve as cladding for the surface of a  
10 glass filament fiber optic transmission line. Examples  
of the latter include  $\text{C}_1$ - $\text{C}_6$  acrylates and methacrylates.

The second hydrocarbyl substituent can also be  
any of the foregoing substituents, provided that the  
second hydrocarbyl substituent is shorter than the first  
15 hydrocarbyl substituent. Preferably, for chromato-  
graphic applications, the second hydrocarbyl substituent  
is sufficiently shorter than the first such that a  
chromatographic support prepared in accordance with the  
present invention having a given first hydrocarbyl  
20 substituent is essentially undistinguishable in its  
chromatographic properties from a conventional silica  
gel support to which is grafted the same given first  
hydrocarbyl substituent. When the first substituent is  
 $\text{C}_{12}$ - $\text{C}_{24}$  alkyl, the second substituent is preferably  
25 alkyl containing 1 to 6 carbon atoms and more preferably  
propyl. When the first hydrocarbyl substituent is  
relatively short, i.e., alkyl containing up to 6 carbon  
atoms, or phenyl, the second hydrocarbyl substituent is  
preferably a shorter alkyl chain (optionally substituted  
30 as described above) or may simply be hydrogen.

In applications of the present invention other  
than the preparation of chromatography supports, the

1 first and second hydrocarbyl substituents can be chosen  
as appropriate to provide any other desired properties  
such as abrasion resistance, translucency, transparency,  
refractive index, light reflectivity (e.g., outside a  
5 fiber optic line), hydrophilicity, hydrophobicity, or  
rheology (for instance, of treated minerals or pigments  
in an emulsion or in an aqueous or non-aqueous liquid  
preparation). In all events, the monolayer prepared in  
accordance with the present invention will impart the  
10 product with the desired ability to resist chemical  
degradation in acidic and basic environments. The  
second hydrocarbyl substituent is preferably one which  
maximizes the ability of the monolayer to prevent  
penetration of acidic and basic substances and ions to  
15 the product surface. Preferred second hydrocarbyl  
substituents are thus alkyl groups containing up to 6  
carbon atoms, optionally substituted with halogen  
(particularly fluorine) or with  $C_{1-3}$  alkyl.

The relative amounts of the first and second  
20 hydrocarbyl substituents on the monolayer are readily  
adjustable, and should be selected to provide the  
desired properties of the product bearing the monolayer.  
For instance, for chromatographic applications it is  
generally preferred that the density of the first  
25 hydrocarbyl substituent be about 2 to about 3 micromoles  
per square meter of silica gel surface, which  
corresponds to about 20 percent to about 50 percent of  
the surface. This permits the second hydrocarbyl  
substituent to "space" the longer substituents from each  
30 other while still retaining the desired protection to  
the substrate and the desired chromatographic  
properties. Accordingly, the mole ratio of first

- 1 hydrocarbyl substituent to the second hydrocarbyl  
substituent on the substrate when it is to be used as a  
chromatographic material will preferably comprise about  
1:1 to about 1:4. It will be recognized that, depending  
5 on the property or properties desired, the mole ratio of  
the first hydrocarbyl substituent to the second  
hydrocarbyl substituent can range from as low as below  
1:100 to as high as 100:1, or higher, although the  
beneficial effects of the second hydrocarbyl substituent  
10 "spacing" the first hydrocarbyl substituents from each  
other are less pronounced as the ratio of first to  
second hydrocarbyl substituents exceeds about 1:1.

- As set forth more fully hereinbelow, the  
relative ratios of the reactants employed to form the  
15 desired monolayer have to be adjusted so as to provide  
the desired ratio of substituents on the monolayer,  
taking into account the fact that the reactants will  
usually react with the substrate at different rates.  
For instance, a smaller reactant such as  
20 propyltrichloro-silane reacts more quickly (and thus  
more of it reacts in a given period of time) than n-  
octadecyltri-chlorosilane. Thus, because of the  
differing reaction kinetics of each reactant, the ratio  
of one to another before reaction will usually not equal  
25 the ratio of one to another on the monolayer following  
reaction. The determination of the relative amounts of  
each reactant to use, in order to obtain a given ratio  
of chain lengths on the monolayer, is a straightforward  
matter for any particular choice of substrate and  
30 hydrocarbyl substituents.

Preparation of articles bearing the monolayers  
described herein is straightforward. The article having

1 surface oxygen is preferably treated to remove  
extraneous materials which might interfere with the  
bonding of the silane reagent to the available oxygen.  
The surface of the article needs to be hydrated, as free  
5 water is essential to achieving the desired reaction  
between the silane and the surface oxygen. However, the  
surface need not and should not carry liquid water in  
amounts that would interfere with the desired  
interaction between the silane and the surface oxygen.

10 It has been determined that the amount of  
water present on the substrate surface affects the  
hydrocarbyl group density that is obtained upon the  
ensuing reaction, and that excessive amounts of reagent  
water lead to decreased hydrocarbyl substituent density.  
15 Accordingly, it is highly preferred that the amount of  
water present at the surface be that which affords the  
densities of 7 or greater, and more preferably 8 or  
greater, micromoles of hydrocarbyl substituents per  
square meter of substrate surface. That amount of water  
20 is generally about equal to the amount (on a mole basis)  
required by the silane reagents employed to form the  
monolayer. Adequate hydration can be provided by  
cleaning and drying the surface of the article to be  
treated and then exposing it to a humid atmosphere so as  
25 to allow a surface monolayer of water vapor to form on  
the article. Alternatively, adequate hydration can be  
provided by adding a known, pre-calculated amount of  
water to a polar solvent in which the hydrocarbyl  
substituents are provided to the reaction site.

30 One technique for applying the monolayer  
employs reactants in a liquid phase. According to this  
procedure, a solution of silanes of the formula  $R^3SiX$ ,

1 and  $R^2SiX$ , is formed in a solvent which is inert to both  
of these silanes and to the article with which the  
reaction will be carried out. In the foregoing  
formulas,  $R^1$  is the first hydrocarbyl substituent,  $R^2$  is  
5 the second hydrocarbyl substituent and X is a leaving  
group which is preferably chlorine, methoxy, or ethoxy.  
(If the second hydrocarbyl desired is hydrogen, the  
corresponding reactant is  $SiHCl_3$ .) Suitable solvents  
include alkanes which are liquid at room temperature and  
10 atmospheric pressure, such as n-hexadecane. The solvent  
is preferably scrupulously anhydrous, to prevent  
premature reaction of the silane with any trace amounts  
of water.

Then, the solution is applied to the surface  
15 on which formation of the monolayer is desired.  
Depending on the nature and size of the article, it can  
simply be immersed in the solution under a suitable  
inert gas blanket to ensure that no atmospheric water  
vapor interferes with the desired interaction between  
20 the article, the reagent surface water, and the silanes.  
No special catalysts or extreme reaction conditions need  
be observed; the silanation reaction generally proceeds  
to completion in a matter of hours. In general, it can  
be expected that slightly raising the temperature of the  
25 reaction mixture will accelerate the completion of the  
reaction. The progress of the reaction can be followed  
in any of a number of conventional ways, for instance by  
monitoring the formation of HX in the solution; when the  
concentration of HX stops increasing, the consumption of  
30 the silane has ceased.

Following the completion of the reaction, the  
thus treated material is removed from the solution,

- 1 washed, and dried. It can then be handled and treated  
in accordance with techniques currently employed with  
analogous materials to which the monolayer has not been  
applied in accordance with this invention. For  
5 instance, silica gel treated in this manner can be  
incorporated into an appropriate column to permit its  
use as a chromatographic packing material. Then, any  
mixture desired to be treated or analyzed chromato-  
graphically is simply applied to the column in a wholly  
10 conventional manner.

- The monolayer can also be applied in the vapor  
phase. The surface to be treated (following surface  
cleaning, as described above) is contacted with a vapor  
which comprises the silanes of the formula  $R^1SiX_3$  and  
15  $R^2SiX_3$ , wherein  $R^1$ ,  $R^2$  and  $X$  are as defined above. The  
vapor may consist entirely of these silanes, or it may  
contain, in addition to those silanes, any other reagent  
intended to be reacted with the substrate surface; and  
the vapor should contain sufficient reagent water vapor  
20 in appropriate relative amounts as described herein to  
provide the desired high density of hydrocarbyl group  
coverage. Also, the vapor may contain as well diluents  
or carrier gas components which will not react with the  
silanes nor with the surface. The vapor should be free  
25 of components which, if present, would undesirably react  
with the surface and interfere with the formation of the  
desired surface layer.

- The silanes can be applied by placing the  
substrate in a chamber containing the silanes.  
30 Alternatively, for a substrate such as a fiber optic  
filament, the fiber can be drawn through such a chamber  
under conditions providing sufficient temperature,

1 circulation of the silanes, and residence time in the  
chamber, such that the desired reaction at the substrate  
surface occurs. Such an application technique permits  
faster treatment times than applications from a liquid,  
5 because there is much less residual drag than is  
inherent in drawing a fiber through a liquid. This  
technique also permits incorporation of other components  
that would also be desirably applied to the surface.  
The vapor-phase reaction is preferably carried out at  
10 temperatures of about 100°C to 140°C.

One advantage of the invention is thus that  
the chain length densities can be arbitrarily varied,  
depending on the final product and properties desired.  
Another advantage is that the final product exhibits no,  
15 or a reduced number, of residual geminal silanols (i.e.  
silicon with two hydroxyl groups).

When the treated material is a mineral or  
pigment, it can be subdivided and added into other  
desired compositions such as paints, cosmetic  
20 preparations, and the like.

It has also been determined that the  
hydrolytic stability of monolayers applied in accordance  
with this invention can be enhanced by a technique which  
converts residual silanol groups present to other more  
25 inert species. Such silanol groups (i.e., -Si-OH  
groups) may be present on the monolayer or on the  
substrate itself and are convertible at either site.

The hydroxyl group of the silanol group is  
converted via a two-step process to a group Z wherein Z  
30 is connected to the silicon atom by a Si-C bond. In the  
first step, the -OH group is replaced by a halide,  
preferably -Cl. In the second step, the halide is

1 replaced with alkyl, preferably C<sub>1</sub>-C<sub>6</sub> alkyl and more preferably methyl.

5 The first step is advantageously carried out by halogenating the silanated material bearing hydroxyl-substituted silicon atoms with a halogenating agent, under anhydrous conditions. A preferred halogenating agent is thionyl chloride (SOCl<sub>2</sub>). Then, the halogenated intermediate that is thus formed is reacted with an alkylating agent, again under anhydrous  
10 conditions. The preferred alkylating agent is a Grignard reagent, preferably an alkylmagnesium bromide such as CH<sub>3</sub>MgBr. The reaction product should then be washed to remove salt byproducts.

This procedure is particularly useful for  
15 "endcapping" material containing a surface of silicon and oxygen atoms, and material comprising a polysiloxanyl monolayer such as that obtained with the present invention, to ensure the absence of Si-OH groups on such surface or monolayer. The Si-C bond that is  
20 created is stable to hydrolytic attack.

The present invention will be illustrated in the following example. This example should be interpreted as illustrative, and not as imparting limitations to the scope of the present invention.

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EXAMPLE 1

Preparation and characterization of a mixed,  
horizontally polymerized bonded chromatographic phase:

5 I. Preparation procedure for chromatographic packing material :

A solution was prepared by mixing n-octadecyl-  
trichlorosilane ( $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$ ) and n-propyltri-  
chlorosilane ( $\text{CH}_3(\text{CH}_2)_2\text{SiCl}_3$ ) in a 4:1 volume ratio in  
10 anhydrous n-hexadecane. (Several other volume ratios of  
the octadecyl to the propyl derivatives in solution had  
been used, including 1:1, 2:1, and 3:1, 8:1 and 3:2; the  
4:1 gave the chromatographic behavior that most closely  
resembled that of a conventional chromatographic  
15 material.) The n-hexadecane has been made anhydrous by  
passing it through a column of dry alumina and silica in  
a glove box having an atmosphere of nitrogen. The  
reagent was kept under the glove box in preparation for  
the reaction with 50  $\mu\text{m}$  silica gel particles. These  
20 silica particles were cleaned in boiling, concentrated  
nitric acid and rinsed with ultrapure water, and dried  
under nitrogen. The surface of the silica particles was  
hydrated by exposure to the vapor of ultrapure water for  
one hour. After this exposure period, the n-hexadecane  
25 solution was mixed with the silica particles and allowed  
to react at room temperature, under nitrogen, for a  
period of one day. The resulting bonded silica  
particles were cleaned by pouring off the n-hexadecane  
and rinsing sequentially with n-hexane, toluene,  
30 acetone, and methanol. Some of this material was used  
to pack a chromatographic column for subsequent study  
with a commercial high performance liquid chromatograph,

1 and some of the material was submitted for analysis by NMR spectroscopy.

II. Characterization of the material by NMR spectroscopy:

5 ✓ A.  $^{13}\text{C}$  NMR

✓ The  $^{13}\text{C}$  NMR spectrum of the material was obtained for the purpose of determining the relative amounts of the  $\text{C}_{18}$  and  $\text{C}_3$  chains attached to the surface. The peak for the first carbon from the silicon  
10 atom, which is common to both the  $\text{C}_3$  and  $\text{C}_{18}$  chains, was four times as large as the peak for the eighteenth carbon from the silicon, which is only contained in the  $\text{C}_{18}$  chains. The ratio of the peak areas revealed  
15 This finding confirmed that the propyltrichlorosilane reacted more quickly with the substrate surface than the octadecyl silane. This mole ratio would be expected to provide, in the silica gel provided with a monolayer according to this invention, the same chromatographic  
20 behavior as a monomeric phase. The reason is that, assuming the total coverage of  $\text{C}_{18}$  and  $\text{C}_3$  is about  $7 \mu\text{mol}/\text{m}^2$ , a 3:1 mole ratio of  $\text{C}_3:\text{C}_{18}$  would correspond to a  $\text{C}_{18}$  coverage of about  $2 \mu\text{mol}/\text{m}^2$ . This is a typical coverage for a silica gel chromatographic material to  
25 which has been bonded individual  $\text{C}_{18}$  chains.

B.  $^{29}\text{Si}$  NMR

The  $^{29}\text{Si}$  NMR spectrum of the material was obtained for the purpose of determining the amounts of unreacted Si-OH bonds in the horizontally polymerized  
30 monolayer. Trifunctional silanes can give rise to multiple -OH groups on silicon atoms after the reaction is complete, and these groups can have a deleterious

1 effect on the chromatographic performance. Providing a  
substituted monolayer in accordance with the present  
invention should result in fewer of these groups.  
Spectra were obtained for the material produced in Part  
5 I and for a conventional polymeric phase (Sander and  
Wise, Anal. Chem. Vol. 56, pp. 504-510 (1984). Based on  
interpretations published in the chemical literature,  
the peaks on the spectra that were obtained were  
assigned to the entities R-Si-(OH)<sub>2</sub>, R-Si-OH and R-Si-O-  
10 Si. A comparison of these two spectra confirmed that  
the product from Part I has fewer groups with the  
structure R-Si-(OH)<sub>2</sub> than does the conventional  
polymeric phase.

III. Chromatographic performance of the material:

15 A. Retention behavior

Chromatograms were obtained using material  
according to the present invention, prepared in  
accordance with Part I, and for a conventional monomeric  
phase comprising the reaction product of chlorodi-  
20 methyloctadecyl silane and silica gel refluxed in  
toluene and end-capped with chlorotrimethyl silane. The  
mobile phase was 70% methanol in water at 30°C, and the  
solutes toluene and benzyl alcohol were used. The  
chromatograms showed that the retention behavior is very  
25 similar for the two columns. This result is consistent  
with the NMR data.

Chromatograms were also obtained for the  
solutes benzo(a)pyrene and phenanthro[3,4-c]phenanthrene  
using a mobile phase of 85% acetonitrile in water. The  
30 retention order of these solutes has been reported to be  
reversed for monomeric and polymeric phases, thus  
constituting a test of whether the mixed phase has

1 selectivity akin to a monomeric or polymeric phase. The  
retention order observed for the mixed column was the  
same as that for the monomeric phase and reversed from  
that of the polymeric phase. (In a "polymeric" phase,  
5 the silica gel is reacted with one compound of the  
formula  $\text{SiCl}_3\text{R}$  under conditions such that a small amount  
of water is intentionally introduced to cause a small  
amount of polymerization of the silane. The resulting  
chains polymerize to form a chain of repeating  $-(\text{Si-O})-$   
10 units which extends from the silica gel surface; no  
monolayer is present as in the present invention.) This  
result observed supports the idea that the chromato-  
graphic phase prepared in accordance with the present  
invention provides the type of selectivity that a  
15 monomeric phase provides.

#### B. Reproducibility

To determine the reproducibility of the  
preparation method, the procedure was followed for  
another batch of silica and silane reagent mixture. No  
20 special care had been taken to pipette exactly the same  
ratio of silanizing reagents as had been used for the  
previous batch, nor was special care taken to prepare  
quantitatively the same mobile phase composition.  
Instead, graduated cylinders were used for dispensing  
25 reagents and solvents. Chromatograms for the separately  
prepared batches were obtained; the averages of 5 runs  
for each column were within 1% of one another.

#### C. Stability to acid hydrolysis

To test the stability toward acid hydrolysis,  
30 a procedure used by a manufacturer of acid-stable  
chromatographic phases was adopted. The mobile phase  
composition was a mixture of 0.5% trifluoroacetic acid

1 in acetonitrile, designated as A, and 0.5% trifluoroacetic acid in HPLC water, designated as B, with the percentages of A and B indicated in the Table below. The flow rate was 2.0 mL/min and the temperature was 50°C. The cycle used is tabulated below.

T0220X

	<u>Time (min)</u>	<u>(A)</u>	<u>(B)</u>
(1)	0.00-6.49	72%	28%
(2)	6.50-15.99	85%	15%
(3)	16.00-25.99	100%	0%
10 (4)	26.00-49.99	0%	100%
(5)	50.00-59.99	72%	28%

Loop back to 0.00 min.

A 100-hour run (which is 100 cycles of the tabulated loop) for the column according to the present invention prepared in accordance with Part I was completed for the tabulated programming of trifluoroacetic acid in water and acetonitrile, using the solute benzo(a)pyrene. Below is a tabulation of the retention time of benzo(a)pyrene after the specified number of hours of mobile phase cycling.

T0221X

	<u>Hours</u>	<u>Retention Time</u>
	0	5.65
	24	5.70
	48	5.68
25	72	5.69
	96	5.67

These data show that there is no change in retention time within the 1% noise on the measurement. The run was continued for another 24 hour period and there was still no change in the retention time. This stability is higher than any known C<sub>18</sub>/silica phase, including both monomeric and polymeric phases.

1 D. Stability to base hydrolysis

Base hydrolysis is the most severe limitation of silica-based chromatographic phases. The stability to base hydrolysis of the column according to the present invention prepared in accordance with Part I was compared to that of the aforementioned conventional monomeric phase, which was end-capped with chlorotrimethylsilane to provide maximum stability. The mobile phase composition was 5% n-propanol in water, with NaOH added to make the pH approximately 12. (A pH of 12.4 at room temperature was measured using a pH meter.) The following cycling was used to monitor the stability to base hydrolysis. The flow rate was 2.0 mL/min and the temperature was 50°C.

- 15 (1) 20 minutes of 5% n-propanol at pH of nominally 12.  
(2) 18 hours of HPLC water  
(3) 20 minutes of 70% methanol in water  
(4) Inject benzyl alcohol and toluene in 70%  
20 methanol in water; measure retention time  
(5) Loop back to Step 1

The capacity factors ( $k'$ ) of benzyl alcohol and toluene after each cycle showed that the monomeric phase degraded more quickly than the phase according to the present invention. More significantly, during the second run of the base solution (step 1) for the monomeric column, the mobile phase was observed to become a milky color, which indicates that the silica substrate began dissolving. The pump pressure was observed to be increasing, therefore, the cycling was discontinued. These same observations were made for another monomeric column. By contrast, no such

- 1 substrate degradation was observed for the mixed phase  
over the entire period of the study which included three  
loops through the cycle. Chromatograms could thus be  
obtained from a column according to the present  
5 invention even after exposure to a substantial volume of  
base.

Additional experiments showed that endcapping  
of the mixed phase provided further improvement in  
stability toward base hydrolysis. The preferred  
10 endcapping reagent is chlorotrimethyl silane;  
chlortri(isopropyl) silane, for example, can also be  
used.

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